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Efficient use of novel hybrid materials in the ultra-trace determination of arsenic from aqueous solutions: an electrochemical study

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ABSTRACT

Hybrid material precursor to a natural bentonite is prepared. Bentonite is modified with hexadecyltrimethyl ammonium bromide (HDTMA) by simple wet cation exchange process as to obtain the organo-modified bentonite (BH). The material is characterized with the X-ray diffraction and IR analytical methods. Moreover, the surface morphology of these solids is discussed with the help of scanning electron microscopic images. Bentonite (B) and hybrid material (BH) is introduced with the carbon powder as to modify the carbon paste electrode (MCPE). The MCPE with reference to B and BH-modified electrodes are then utilized to study the electrochemical behavior of arsenic(III) from aqueous solutions. Characteristic reversible behavior of arsenic(III) is obtained by the cyclic voltammetric measurements. An enhanced cathodic or anodic current is obtained using the BH-modified electrode comparing to the B-modified electrode. Further, the study is extended with a wide range of scan rate (80–200 mV/min) and the effect of pH (2.5–8.5). The concentration dependence study clearly reveals that reasonably a good linearity of cathodic current is obtained for the As(III) concentration ranging from 1.0 to 40.0 μg/L using BH-modified electrode. Moreover, the limit of detection and limit of quantification (LOQ) is obtained for arsenic(III) detection using the calibration equation. The study is further extended for the detection of arsenic(III) in presence of several cations viz., Cu(II), Mn(II), Pb(II), Cd(II), and Fe(III) and anions phosphate, glycine and EDTA independently using the BH-modified electrodes.

Keywords: Hybrid materials; Ultra-trace; Arsenic(III); Electrochemical sensor; Co-existing ions

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1. Introduction

The crystal structure of clay and minerals consists of sheets which are firmly arranged in a certain structural layers. The individual layer is composed of two, three or four sheets. The sheets are made with tetrahedral $[SiO_4]^{4-}$ (T) and octahedral $[AlO_3(OH)_3]^{6-}$ (O) units. The interiors of these sheets are contained with smaller cations and their apices are occupied by oxygen from which some are bonded with protons (–OH). All this fundamental structural unit is arranged to form a hexagonal network with each sheet [1,2]. Bentonite is natural clay containing mostly smectite and kaolinite group of clays. The group of smectite is found to contain strongly expanding three-sheet

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phyllosilicates, where the T:O ratio is 2:l and the charge of the three-sheet layer (unit cell) is 0.5–1.2 e/uc (negative charge). This arises from the isomorphous substitution of Al^{3+} and Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} in the octahedral sheet, whereas the kaolinite and serpentine group are a typical two-sheet phyllosilicates, where the T:O ratio is 1:1 and the charge of the two-sheet layer (unit cell) is 0 e/uc, since bentonite contains, dominantly, the smectite mineral phase. Moreover, the smectite possesses permanent negative charge which is naturally compensated by exchangeable cations (i.e. Na^+, K^+, Mg^{2+}, Ca^{2+}, etc.). These exchangeable cations are located within the interlayer space of bentonite sheets [3]. Therefore, bentonite shows fairly a high cation exchange capacity (CEC), makes it good water replace swelling type mineral. Additionally, a high specific surface area leads mineral a strong adsorption/absorption capacity towards several ionic or polar compounds.

Although bentonite is a good porous and hydrophilic material, it shows significant affinity towards several heavy metal toxic ions [4–7]; however, this possesses insignificant affinity towards the anionic species or the non-polar or slightly-polar organic impurities. However, bentonite contains several exchangeable cations, this makes possible to exchange these inorganic cations with organic cations and to obtain the organo-modified hybrid materials. These hybrid materials show significant affinity towards several oxyanions including the arsenic and non-ionic organic compounds from aqueous solutions as the introduced long-chain organic cation provides a hydrophobic core with enhanced organophilicity [8].

The presence of arsenic is ubiquitous in natural environment. It is distributed in air, soil, and water [9,10]. At places, the ground water of Bangladesh, India, USA, China, Mexico, Taiwan, etc. is greatly contaminated with arsenic. It was reported that more than 100 million people are affected greatly with arsenic poisoning around the globe [11–13]. The inorganic arsenic compounds are classified as Group 1 carcinogen (carcinogenic to humans), demonstrated by the International Agency for Research on Cancer. This is based on sufficient input data for carcinogenicity in humans [14,15]. A long-term exposure or intake of arsenic causes for lung, liver, kidney, bladder, and skin cancer as well the pigmentation changes, skin thickening (hyperkeratosis), neurological disorders muscular weakness, loss of appetite, nausea, etc. [8,16–18]. Therefore, based on the acute toxic effects of arsenic, the regulatory bodies viz., World Health Organization (WHO) and United States Environmental Protection Agency (US EPA) has recommended to reduce the arsenic level from 50 to 10 μg/L in the drinking water. Because of such stringent regulatory standards, there is a need of developing suitable and robust analytical tool to determine arsenic from aqueous samples at ultra-trace levels. There are several but sophisticated techniques developed viz., electro thermal atomic absorption spectroscopy [18,19], hydride generator-coupled atomic absorption spectroscopy [20], or atomic fluorescence spectroscopy [21], mass spectrometry with inductively coupled plasma [22], electrochemical methods [23,24], spectroflurimetry [25], laser-induced breakdown spectroscopy [17], CPE-FAAS [26], etc. Similarly, the neutron activation analysis, ion chromatography, and gas chromatography are also described with varying degrees of detection limit [27]. Although, these techniques are efficient and show high precision, but are found to be extremely expensive and a pre-concentration step is also needed, which is difficult to make it available for several under developed countries. Moreover, the greatest drawback of most of these analytical methods is applicable for on-site or real-time analysis. Therefore, there is a greater demand of analytical method to be developed which could easily be operated on-site, show cost effectiveness, and provide ultra-trace level detection.

Electrochemical sensors, in recent time, find greater attention in detection and determination of several pollutants at trace to ultra-trace levels [28–31]. Moreover, the electrochemical devices based on the carbon paste electrode (as working electrode) could show several advantages viz., as low background currents, reproducible results, simple surface renewability, easy fabrication, and modification with wide range of compounds [29]. Therefore, the present communication deals with simple modification of carbon paste electrode with the HDTMA-modified bentonite hybrid material and this is further utilized in the ultra-trace determination of arsenic(III) from aqueous solutions.

2. Experimental

2.1. Reagents

Bentonite clay was procured from commercial supplier which was mined from Bhuj, Gujarat, India. It was crushed and sieved to obtain 100 BSS (British Standard sieve i.e. 0.150 mm) mesh size. The powder of bentonite was washed with purified water and dried at 90˚C in a drying oven. CEC of the bentonite was determined using standard US EPA method 9080 (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9080.pdf), and this was found to be 69.35 meq/100 g of bentonite. Hexadecyltrimethylammonium bromide (HDTMA), carbon powder (glassy spherical powder 2–12 μm), and titanium wire (0.81 mm) were procured from the Sigma-Aldrich, USA. Cadmium nitrate tetrahydrate, copper(II) sulphate pentahydrate, and lead nitrate were obtained from Merck India. Ferric nitrate nonahydrate (AR), manganese(II) chloride tetrahydrate (AR), and paraffin oil were procured from HiMedia Chemicals, India. Sodium metaarsenite was obtained from Wako Pure Chemical Industries Ltd, Japan. The deionized water is further purified (18 MΩ cm) using the Millipore water purification system (Milli-Q+).

2.2. Methodology

2.2.1. Preparation and characterization of HDTMA-bentonite

Bentonite was modified by hexadecyltrimethylammonium bromide by simple wet cation exchange process. The detailed description of preparation process was described elsewhere [32].

Further, the samples bentonite (B) and HDTMA-bentonite (BH) were characterized by the X-ray diffraction (XRD) data as collected by XRD machine (PANalytical, Netherland, Model X'Pert PRO MPD). FT-IR (Bruker, Tensor 27, USA by KBR disk method) was used taking the IR data of B and BH solids. Surface morphology of BH hybrid material along with the bentonite was obtained taking the scanning electron microscopic images using a scanning electron microscope (Model FE-SEM (Field Emission Scanning Electron Microscope, Model S-4700, Hitachi, Japan).

2.3. Apparatus

All electrochemical studies were conducted using a Potentiostat/Galvanostat (BioLogic Science Instruments, France, Model: SP 50). The electrochemical output data was analysed using the ECLab® computer software. A conventional single compartment three electrodes cell assembly was employed having Ag | AgCl reference electrode (BASi, USA, model: RE-5B) and platinum electrode as an auxiliary electrode. The modified carbon paste electrode was prepared and used as working electrode. Moreover, the electrical circuitry was made with the help of titanium wires. A pH-meter having glass and calomel electrode assembly (EUTECH instruments PC 510, pH/conductivity/TDS/C/F meter) was used for entire pH measurements in aqueous solutions.

2.4. Fabrication of working electrode

Carbon paste electrode was employed as working electrode with its suitable modification. The modification of carbon paste electrode was carried out as: 6 g carbon powder + 1.0 g of BH or B + 1.0 g of paraffin oil were intimately mixed in a Petri dish using a Teflon spatula. The paste prepared was introduced manually to pack tightly a 4 cm long Teflon tube (inner diameter 4.2 mm). One end of this tube is sealed with Teflon tape and very carefully a titanium wire (0.81 mm) was inserted from this end of the tube. The other end of the tube was kept open to expose the surface for electrochemical reactions. The surface of the tube was polished with a glassy paper. Also, at the completion of each experiment, the open end of the tube was cut by a sharp knife to get an unexposed active surface. The working electrode was dipped into the test solution for 10 min prior to conducting the electrochemical measurements. Further, the dissolution of carbon paste was also observed in the bulk solution by simple filtration which showed that almost a negligible amount of carbon was occurred onto the 0.25 μ filter paper.

2.5. Cyclic voltammetric measurements

The electrochemical measurements are carried out using cyclic voltammetry working with the EC-Lab software connected to the personal computer. A conventional 100 mL electrochemical cell is employed, using a three-electrode arrangement. B/or BH-modified carbon paste electrodes (MCPE) were used as working electrode. A platinum electrode was employed as an auxiliary electrode and the Ag | AgCl electrode was used as reference electrode.

A stock solution of arsenic(III) (100 μg/L) was prepared using the 1.0 M KNO_3 solution. Further, the arsenic(III) test solution of required concentration was prepared in 1.0 M KNO_3 electrolyte solution whose pH was adjusted using 0.1 M HNO_3 and 0.2 M NaOH solutions by successive dilution of stock solution. The test solutions were deoxygenated with a stream of high purity nitrogen gas (99.99%) at least for 10 min prior to each electrochemical scan. The cyclic voltammograms were obtained with an exciting potential applied in a saw tooth manner within a wide potential range ±1.0 V against an Ag | AgCl reference electrode. The exciting signal was, at different scan rate i.e. 80–200 mV/s, applied to assess the scan rate dependence study. The other measurements were conducted at a constant scan rate of 100 mV/s. The electrochemical data were obtained for six replicate samples and the error was mentioned with ±3σ values. Moreover, some trials were repeated using different electrodes.

3. Results and discussion

3.1. Characterization of materials

The hybrid materials BH along with the bare bentonite were characterized by the FT-IR and XRD methods, and results were well discussed elsewhere. Similarly, the surface morphology of these solids was discussed with the FE-SEM images of these solids [32].

3.2. Cyclic voltammetric studies

The cyclic voltammograms (CV) were obtained for the As(III) using the B/and or BH MCPE; employed as working electrode. The CV was obtained at pH 2.5 and presented graphically in Fig. 1. It is evident from the figure that no significant difference in the CV pattern is obtained in presence of B and BH solid modified carbon paste electrode. However, a substantial increase in current is obtained for the oxidative and reductive peaks of As(III) employing the BH-modified CPE. This shows that arsenite possess relatively a higher affinity towards the BH solid comparing to the unmodified bentonite. Similarly, the ΔE_p as measured for the dominant peak for BH modified and B-modified samples are found to be 0.12 and 0.27 V, respectively. Therefore, these results again show that the arsenic(III) is attached specifically onto the electrode surface, enabling fair and enhanced response, which is then utilized in sensor development. Moreover, the modification of electrode with BH causes the charge transfer at the interface of electrode easier and faster comparing to the B-modified electrode [33]. Relatively, the low value of ΔE_p further indicates that the redox behavior of arsenic is reversible in nature [24].

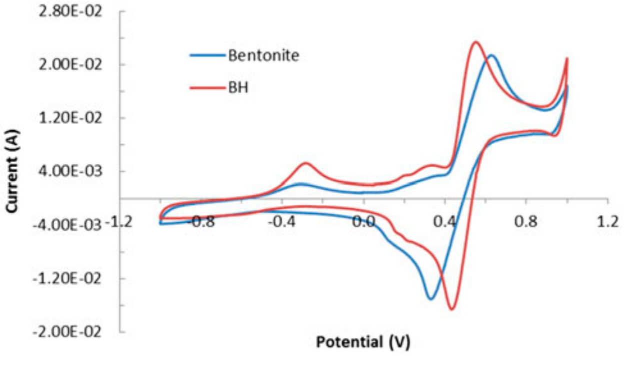

Fig. 1. Cyclic voltammograms of arsenite(III) using modified and unmodified bentonite samples at pH 2.5, 1.0 M KNO_3 and at scan rate 100 mV/s.

3.3. Effect of scan rate

The CV is obtained at varied scan rates (i.e. 80–200 mV/s) keeping constant arsenic(III) concentration 50.0 μg/L and at constant pH 3.5 and 1.0 M KNO_3 background electrolyte solution. The results are presented graphically in Fig. 2(a) and (b), respectively for the B and BH-modified electrodes. It is evident that increasing the scan rates causes an apparent increase in peak current (both cathodic and anodic) (A). Further, the current is significantly higher for the BH-modified electrode than B-modified electrode. These results again suggest that surface reactions are easier and faster at the BH-modified working electrode. The results also pointed that the surface area of BH-modified electrode is relatively higher than the B-modified electrode, which apparently enables to increase the sensitivity of the electrode for redox behavior [34]. Further, the reductive peak current

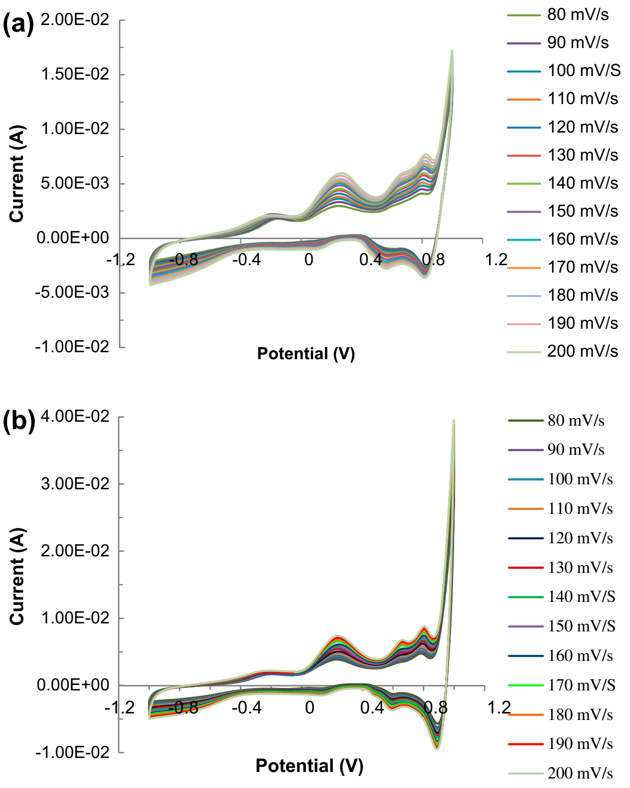

Fig. 2. Electrochemical behavior of arsenic(III) as a function of scan rate at pH 3.5 using (a) B-modified and (b) BH-modified carbon paste electrodes.

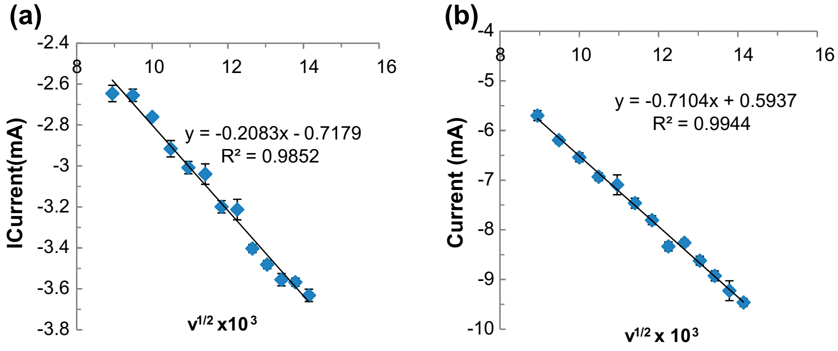

Fig. 3. Plot of cathodic current as a function of $v^{1/2}$ (v: scan rate) using (a) B-modified and (b) BH-modified carbon paste electrode.

(mA) is plotted against the square root of scan rate (Fig. 3(a) and (b)). Reasonably, a good linearity is achieved between current (I_m) vs. $v^{1/2}$ (v: scan rate). The linear regression equations are obtained as: $I_m = -0.2083v^{1/2} - 0.7179$ ($R^2 = 0.9852$) and $I_m = -0.7104v^{1/2} + 0.5937$ ($R^2 = 0.9944$), respectively for the B and BH-modified working electrode for As(III). These results indicate that the reduction of arsenic species is diffusion-controlled process at slow scan rate [35]. Further, the electrochemically active surface area is obtained using the Randles–Sevik equation (Eq. (1)):

$$I_m = 2.69 \times 10^5 \cdot n^{3/2} \cdot v^{1/2} \cdot D^{1/2} \cdot C \cdot A \tag{1}$$

where I_m is the peak cathodic current (A); n is the number of electrons involved in reduction; D is the Diffusion coefficient of arsenic (cm^2/s); v is the scan rate (V/s); C is the concentration of arsenic (mol/L); and A is the electroactive area of working electrode (cm^2). The slope of the straight line obtained (vide Fig. 3) could help in obtaining the surface area of electrode (A). The diffusion coefficient of As(III) in water is taken as reference value which was reported to be 11.6×10^{-6} cm^2/s for the As(III) [36]. Based on this, the surface area of the working electrode is calculated and found to be 2.076 and 0.609 cm^2 for the As(III). Moreover, the electroactive surface area of working electrode deduced with this method is intended to relate the amount of electroactive sites available on to the electrode [37]. These results clearly indicated that the surface area of working electrode is significantly increased (more than three times) in the presence of BH solid comparing to the B solid. Therefore, the electrode could have possible application in the ultra-trace determination of As(III) from aqueous solutions. The similar results are reported previously where exfoliated graphite electrode was modified with bismuth nanoparticles enhanced the surface area of electrode at least in the arsenic determination [33].

3.4. Effect of pH

The effect of pH in redox behavior of arsenic(III) with BH-modified electrode is studied at various pH values i.e. from 2.5 to 8.5 in 1.0 M KNO_3 solutions and at 200 mV/s scan rate. The CV scans are obtained applying the potential ±1 V against the Ag|AgCl reference electrode. The CV is presented in Fig. 4 for arsenic(III). Fig. 4, clearly demonstrates that a sharp oxidative peak is appeared at around an applied potential of −0.35 V at studied pH 2.5 and 3.5. A similar peak is centred on the applied potential of *Ca* 0.23 V at other pH conditions i.e. pH 4.5–8.5. This suggests that the oxidation of arsenite took place in step from As(0) to As(III). It is to be noted that at pH 2.5–8.0 the dominant species of As(III) is the neutral

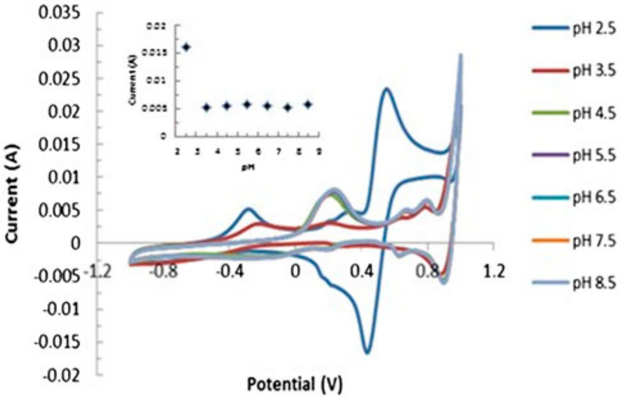

Fig. 4. Electrochemical behavior of arsenic(III) as a function of solution pH using BH-modified carbon paste electrode.

H_3AsO_3 species (pK_a 9.29). However, at pH 10.0 the dominant species could be $H_2AsO_3^-$. The detailed speciation of As(III) as a function of pH was conducted and presented elsewhere [38]. Therefore, the possible oxidation of the As(III) could be ascribed with the three electron liberation reaction as:

$$As(0) + 3H_2O \rightarrow H_3AsO_3 + 3e + 3H^+ \quad (2)$$

$$As(0) + 2H_2O \rightarrow AsO_2^- + 3e + 4H^+ \quad (3)$$

Further, it is observed that at highly acidic conditions i.e. pH 2.5 another sharp peak is observed at around applied potential 0.6 V, whereas, almost at the same applied potential, less dominant peak is appeared for pH 3.5 or 4.5. This peak, perhaps, represents the further oxidation of As(III) to As(V) which is favored at highly acidic conditions. However, at moderate to higher pH values this peak is less dominant or not pronounced. The oxidative reaction of As(III) to As(V) may be ascribed to a two-electron liberation oxidation as:

$$H_3AsO_3 + H_2O \rightarrow H_2AsO_4^- + 2e + 3H^+ \quad (4)$$

Or

$$H_3AsO_3 + H_2O \rightarrow HAsO_4^{2-} + 2e + 4H^+ \quad (5)$$

Similarly, the reverse sweep of the cyclic voltammograms at highly acidic condition, i.e. at pH 2.5 shows a sharp reduction peak at around applied potential 0.45 V, suggesting that the reduction of arsenate took place in step from As (V) to As(III) state. This process is followed by another broad weak reduction peak at around potential −0.2 V, which indicates the reduction of As(III) to As(0). In other words, the corresponding reduction of the arsenic indicates that the electrochemical process is reversible in nature. Similarly, the voltammograms obtained at moderate to neutral pH conditions show two-step reduction i.e. possibly As(V) to As(III) and As(III) to As(0) as a sharp peak is observed at an applied potential of around 0.89 V and small and broad peak is observed at −0.3 V. It was previously reported that As(III) showed characteristic reductive peak at −0.35 V (vs. SCE), indicated for the three electron reduction of As (III) to As(0), and with the reversal scan, a similar oxidative peak observed at +0.25 V (vs. SCE), which was due to the oxidation of As(0) to As(III) onto the gold nanoparticle modified indium tin oxide (ITO) film coated glass electrode at highly acidic conditions [39].

Further, the pH dependent electrochemical response is ascertained using the reductive peak current ($|I_m|$) (at 0.45 V at pH 2.5 and 0.89 V at pH 3.5–8.5) and presented graphically in Fig. 4 (inset). Fig. 4 clearly shows that the peak current is relatively high at pH 2.5 for As(III). However, within the pH region 4.0–8.5, the peak current is almost independent of pH. These, results indicate that the estimation of arsenic is, perhaps, feasible in the wide range of pH.

3.5. Concentration dependence studies

The concentration dependence study is conducted at varied arsenic(III) concentrations from 1.0 to 40.0 μg/L at pH 3.5, 1.0 mol/L KNO_3 solutions. The scan rate is kept constant 200 mV/s and it is scanned within the potential range ±1 V. Both the B-modified and BH-modified electrodes are employed and the results are presented graphically in Fig. 5(a) and (b), respectively for the B and BH-modified electrodes. A characteristic reductive peak occurred around the

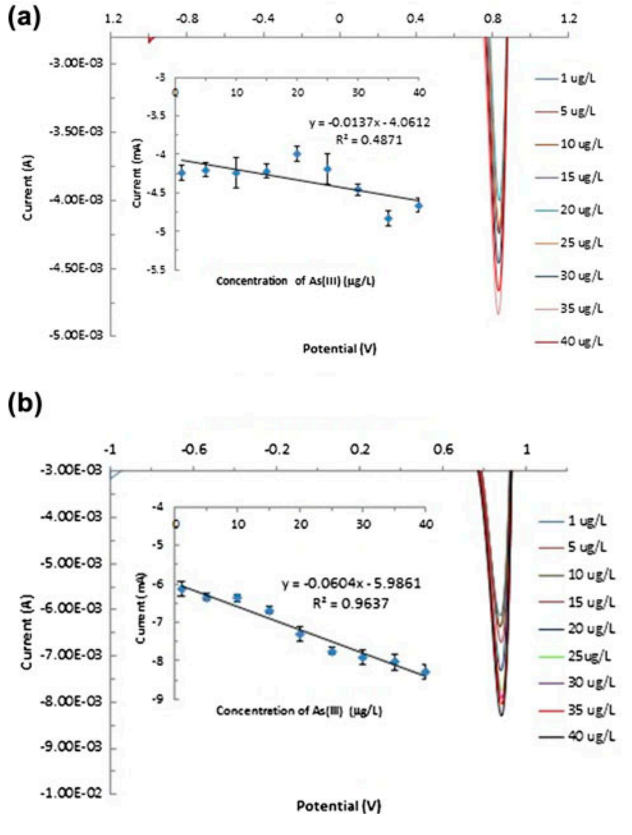

Fig. 5. Electrochemical determination of arsenic(III) using (a) B-modified and (b) BH-modified carbon paste electrode (u stands for μ).

applied potentials of +0.88 and +0.83 V, respectively, for the BH and B-modified electrodes for As(III) at pH 3.5 (Fig. 5). The reductive peak is then utilized to obtain the calibration line and it is found that fairly a good linear relationship is obtained between the reductive peak current and the concentration of arsenic(III) within the studied concentration range of 1–40 μg/L for BH-modified electrode. The calibration line is represented as $I_m = -0.0613 \times 10^{-3}$ C (μg/L) − 5.973×10^{-3} ($R^2 = 0.974$) (inset Fig. 5(b)). However, the B-modified electrode shows somewhat distorted relationship for the similar reductive peak current as the straight line equation was found to be $I_m = -0.0137 \times 10^{-3}$ C (μg/L) − 4.061×10^{-3} ($R^2 = 0.487$) (inset Fig. 5(a)) with very low correlation coefficient value. These results pointed that electrochemical sensor obtained with the BH-modified working electrode is an useful tool to be employed for the ultra-trace level detection of arsenic(III) from aqueous solutions.

Further, the limit of detection (LOD) and limit of quantification (LOQ) were obtained with the equations 3 × S.D./m and 10 × S.D./m, respectively, where S.D. stands for the standard deviations of the blank sample ($n = 6$) i.e. arbitrarily taken 25 μg/L As(III) solutions and "*m*" is the slope of the calibration curve. The LOD and LOQ values were found to be 2.04 and 6.79 μg/L, respectively. The low value of LOD again indicated the applicability of this material in the low-level detection of arsenic(III) from aqueous solutions. The other studies using the carbon nanotube or polymeric resin-modified carbon paste electrode employed mineral oil and silicone as binder separately. Further, the electrode is employed as working electrode in the electrochemical detection of arsenic from sugarcane brandy. LOD and LOQ were found to be 10.3 and 34.5 μg/L for mineral oil and 3.4 and 11.2 μg/L for silicone using the carbon nanotube modified electrode [40]. Similarly, the visible spectroscopic technique was employed using the functionalized gold nano-particles in the detection of arsenic from aqueous solutions, and the LOD and LOQ values are reported to be 2.5 and 8.4, respectively [15]. Similarly, the other study showed reasonably a low detection limit (3 ppb) for As(III) was obtained using the gold plated carbon paste electrode [41]. An extremely low LOD i.e. 0.3 μg/L for As(III) was obtained using gold nanoparticle modified ITO film coated glass electrodes in an anodic stripping voltammetry [42].

3.6. Effect of co-existing ions in the estimation of As(III)

The influence of cations viz., Cu(II), Pb(II), Cd(II), Mn(II) and Fe(III) and anions viz., PO_4^{3-}, EDTA, and glycine in the estimation of As(III) (30.0 μg/L) at pH 3.5 was studied and results are tabulated in Table 1. The experiments were performed varying the As(III) concentration from 1.0 to 40.0 μg/L in 1.0 mol/L KNO_3 solutions at pH 3.0 and at scan rate 100 mV/s. Further, the calibration line was obtained with the linear regression equation, $I_m = -0.052 \times 10^{-3}$ C (μg/L) − 0.012. The oxidation and reduction peaks of As(III) were unchanged with the addition of interfering ions. Moreover, the concentration of the ions added to As(III) was calculated using the straight line equation obtained from As(III), which gave good correlation with the theoretical value, indicating that the presence of these cations (except Cu(II) and Fe(III)) did not affect significantly the determination of As (III). Similarly, the anions also did not affect the detection of As(III) from the aqueous solutions. Earlier, the Cu(II) interference was significantly suppressed using the silicone oil-based carbon paste plated with gold Au(C/SO) electrode and analysed with constant current stripping analysis [40]. However, highly sensitive electrochemical methods based on the linear sweep voltammetry and square wave voltammetry with gold nanoparticle modified electrode provided the LOD of 0.0096 and 0.014 ppb, respectively. But, the methods are restricted for the arsenic detection in the natural matrix of water in presence of Cu(II) [43].

Table 1
Concentration of As(V) in presence of interfering ions calculated from the calibration line of As(III) (1.0–40.0 μg/L)

Interfering ions	Concentration
As(III)	30.00 ± 0.80
Cu(II)	26.35 ± 0.75
Mn(II)	32.00 ± 0.45
Pb(II)	28.49 ± 0.56
Cd(II)	28.94 ± 0.89
Fe(III)	38.31 ± 0.99
PO_4^{3-}	32.10 ± 0.68
EDTA	28.79 ± 0.85
Glycine	31.70 ± 0.90

4. Conclusions

HDTMA-modified bentonite hybrid material (BH) is obtained by simple wet cation exchange process. The IR data indicates that HDTMA is introduced with the bentonite, whereas XRD data enables that bentonite possesses with quartz, smectite, kaolinite, and illite mineral phases. The surface morphology shows disordered and heterogeneous surface structure of the BH solid. Further, the bentonite (B) and hybrid material (BH) is introduced with the carbon powder as to modify the carbon paste electrode (MCPE). The MCPE with reference to B and BH-modified electrodes are utilized in the electrochemical behavior of arsenic (III). A characteristic reversible behavior of arsenic(III) is recorded by the cyclic voltammetric measurements. Moreover, a significantly enhanced cathodic or anodic current is obtained using the BH-modified electrode comparing to the B-modified electrode. Also increasing the scan rates from 80 to 200 mV/s shows an apparent increase in oxidative or reductive current. This is further utilized to estimate the electroactive surface area of working electrode, which is found to be 2.076 and 0.609 cm^2, respectively, for BH and B-modified carbon paste electrode. pH (2.5–8.5) dependence electrochemical behavior of arsenic(III) is obtained. The concentration dependence study clearly reveals that reasonably a good linearity of cathodic current is obtained for the arsenic(III) detection in the concentration range 1–40 μg/L As(III) using BH-modified electrode having the calibration line $I_m = -0.0613 \times C \ (\mu g/L) - 5.973$. On the other hand, the bentonite-modified electrode shows a poor linearity for the studied arsenic(III) detection. The LOD and LOQ is found to be 2.04 and 6.79 μg/L, respectively, using the BH-modified carbon paste electrode in the detection of arsenic(III) from aqueous solutions. Further, the presence of cations Cd(II) and Pb(II) Mn(II) anions phosphate, glycine, and EDTA could not affect the detection of arsenic(III), whereas Fe(III) and Cu(II) could affect significantly its determination. Therefore, the use of natural bentonite in the preparation of hybrid materials could have greater application in the ultra-trace determination of arsenic(III) from aqueous solutions.

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